MICROWAVE SPECTROSCOPY AND MOLECULAR STRUCTURE OF ISONITROSYL HYDROXIDE (HOON)

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Nitrous acid (HONO) is an important member of the atmospheric nitrogen cycle whose chemistry involves a variety of gas-phase, photochemical, and heterogeneous processes. Among its formation pathways in the atmosphere is the ternary association of hydroxyl (OH) with nitric oxide (NO), but the formation of the isonitrosyl hydroxide (HOON) isomer has largely been ignored owing to early theoretical studies that questioned its stability. Guided by new high-level ab initio calculations, we have detected the rotational spectrum of *trans*-HOON in an electrical discharge of a dilute mixture of NO and water vapor by a combination of Fourier transform microwave spectroscopy and double resonance methods. No evidence for the *cis* isomer was found in any of our spectroscopic surveys between 15.4–17.0 GHz. A semi-experimental equilibrium structure for *trans*-HOON has been derived to high precision from isotopic substitution (DOON, $H^{18}OON$, $HO^{18}ON$, $HOO^{15}N$) along with zero-point vibrational corrections calculated at the CCSD(T)/aug-cc-pVTZ level of theory. Most notably, the central O–O bond in *trans*-HOON is found to be 1.9149 ± 0.0005 Å in length, which is the longest known O–O bond in a molecule (nearly 20% longer than the analogous bond in the HOOO radical).